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(54) Title: CLOSURES FOR CONTAINERS FOR WINE OR WINE-BASED PRODUCTS (57) Abstract A closure for a container of wine or a wine-based product which can replace a conventional cork and provide a good barrier against ingress of oxygen, is in the form of a stopper moulded from an ethylene/vinyl acetate copolymer with a vinyl acetate content of from 10% to 25%, the stopper having a closed-cell foamed core (which may contain water and sulphur dioxide to act as an oxygen scavenger) and a liquid-impervious skin, the degree of foaming being from 45% to 70%. The preferred VA content is from 10% to 20%. The stopper is preferably coated with a silicone lubricant.		

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CLOSURES FOR CONTAINERS FOR
WINE OR WINE-BASED PRODUCTS

This invention relates to closures for containers for wine or wine-based products. Traditionally such closures have been of cork, in the form of bungs or stoppers inserted into the necks of glass bottles. Cork has the advantages of high elasticity, resilience and softness, which enable cork stoppers to be compressed to a diameter less than that of the bottle neck for insertion into the neck and then to recover elastically to such an extent as to seal the neck effectively. The frictional characteristics of cork are such that the stopper grips the neck tightly and is not liable to accidental displacement but can be drawn out when required and the gas barrier characteristics are such that a cork stopper of conventional size, having a length of 38 mm or 44 mm and a diameter when uncompressed of 22 mm (19 mm when compressed in a bottle neck), will restrict ingress of oxygen into the bottle to a low figure. Against these advantages, one must set the disadvantages that cork, being a natural product, is variable in quality, and good quality cork suitable for stoppers is relatively expensive. Any defects in the cork may lead to deterioration in the effectiveness of the stopper and deleterious effects on the taste of the contents.

For the preservation of wine and wine-based products, it is essential that access of oxygen to the product should be restricted, to prevent oxidation of the flavour constituents and of the alcohol content. To stabilise the product against oxidation, it is normal practice for the producer to incorporate a small proportion of free sulphur dioxide (SO_2) in the product, though the amount which may be incorporated is restricted by law. Thus a light table wine may, for example, contain 50 parts per million of free SO_2 . To achieve an adequate shelf life for the wine, say one year for a mass-produced light table wine, the



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bottle and stopper must co-operate to restrict access of oxygen to the wine to a total amount during that year which is less than the total amount which can be dealt with by the SO_2 in the wine. For a wine contained in a standard
5 75 centilitre bottle and incorporating 50 p.p.m. SO_2 , it can be calculated that the amount of oxygen which can be dealt with by the SO_2 in the wine is 6.5 ml at normal temperature and pressure.

Efforts have been made previously to produce stoppers
10 for wine bottles from synthetic plastics materials, in particular polyolefins such as polyethylene. Difficulties have been encountered, however, because these materials are too hard and incompressible for a solid stopper to be easily inserted into a bottle neck or to conform with
15 irregularities in the interior surface of the neck to produce a good seal, when inserted. It has been proposed that such stoppers should be made with hollow interiors or in the form of a closed-cell elastic foam with a densified periphery offering a smooth external surface,
20 in order to make them more compressible, but the relative lack of resilience in the material still makes it difficult to achieve sufficient conformity with irregularities in the neck to produce a good seal. Further, the material has a relatively low creep resistance so that such
25 stoppers tend to take a permanent set after insertion into a bottle neck and thereby lose their grip in the neck after a time. The frictional characteristics of the material are such that the stopper can then slide out of the neck.

30 In our prior co-pending British Patent Application No. 17415/76, we have described and claimed a closure for a container of a wine or a wine-based product, at least a part of said closure intended to contact the product being in the form of a moulded stopper of a thermoplastics
35 material, such as an ethylene/vinyl acetate copolymer, having a foamed core within a liquid-impervious skin, wherein the foamed core has been produced by blowing the



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thermoplastics material with a blowing agent including a thermally decomposable sulphite and a water-producing compound, whereby said foamed core contains sulphur dioxide and water enabling the sulphur dioxide to act as
5 an oxygen scavenger.

It is an object of the present invention to provide closures for containers for wine or wine-based products which will avoid the above-mentioned disadvantages and specifically to provide closures for synthetic plastics
10 materials which can be made at relatively low cost and which will have the advantages of natural cork closures as regards insertion and retention of the closures, without the disadvantages described above.

According to the invention, there is provided a
15 closure for a container for a wine or wine-based product, at least the part of said closure which is intended to be exposed to the product being in the form of a moulded stopper of a thermoplastic material having a closed-cell foamed core within a liquid-impervious skin, wherein the
20 thermoplastic material is an ethylene/vinyl acetate copolymer with a vinyl acetate content of from 10% to 25% and the degree of foaming of the moulded stopper, measured in terms of the reduction of density as compared with the unfoamed material, is from 45% to 70%.

25 Preferably the ethylene/vinyl acetate copolymer has a vinyl acetate content of from 10% to 20%.

It has been found that by selecting the material and the degree of foaming in this manner the stopper can be made to reproduce the desirable properties of natural cork
30 as regards compressibility and resilience, so that it is readily inserted into the neck of a container, such as a bottle, and conforms with any irregularities therein so as to produce a good seal. The material has a good creep resistance so that the stopper retains its grip in the neck
35 and is not liable to be accidentally dislodged. Stoppers in accordance with the invention, when made of appropriate conventional size, can thus be employed with existing cork

BUREAU

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inserting machinery in bottling plants.

By selecting the material to have a vinyl acetate content within the specified range, it has also been found possible to achieve satisfactory gas barrier characteristics for restriction of ingress of oxygen into the container. In particular, where the moulded stopper is of conventional dimensions for a wine bottle cork, having a length between 30 mm and 50 mm and an uncompressed diameter of substantially 22 mm, it has proved possible to provide an oxygen barrier sufficient to restrict passage of oxygen into a container in which the closure is fitted to less than 4 ml per annum.

The oxygen barrier can be further improved by arranging that the cells of the foamed core contain sulphur dioxide and water enabling the sulphur dioxide to act as an oxygen scavenger. This can be done as described and claimed in our co-pending British Patent Application No. 17415/76, by producing the foamed core by blowing with a blowing agent including a thermally decomposable sulphite and a water-producing compound.

To achieve desirable frictional characteristics and thereby facilitate handling of the closures in existing cork-inserting machinery, it is preferable to coat the moulded stoppers with a lubricant.

The lubricant must be insoluble in water, because water-soluble lubricants could mix with the product in the container and allow the stopper to slide in the neck. It is also important that the lubricant should not migrate into the body of the stopper and thus be lost from the surface. The preferred lubricant which is coated on to the moulded stopper is a silicone, specifically a polymethyl siloxane, which is insoluble in water and remains on the surface of the stopper.

Specific examples of the invention will now be described by way of example.

Cylindrical stoppers similar to conventional wine corks, having a length of 38 mm and a diameter of 22 mm,



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were formed from three different ethylene/vinyl acetate (EVA) copolymers having vinyl acetate (VA) contents of 12½%, 15% and 18%, respectively. An injection moulding technique was used in which the EVA copolymer was mixed
5 with a blowing agent, heated and injected into a cool mould so as to produce in known manner a stopper having a closed-cell foamed core within a smooth liquid-impervious skin. The melt flow index values for the EVA copolymers were 4, 8 and 10 respectively. It is believed
10 that the melt flow index is not particularly relevant in this context, though excessively fluid copolymers should be avoided because of difficulty of ensuring formation of the desired multiplicity of small closed cells and avoiding cell collapse in the foaming process. The feed-
15 stock was formulated and the blowing controlled to achieve a degree of foaming of from 50% to 70% measured in terms of the reduction in density as compared with the unfoamed material. The degree of foaming has been found to be critical. Below 45% foaming the stopper is
20 insufficiently soft and compressible and a minimum of 50% is usually to be preferred, whereas above 70% the skin of the stopper is too thin to retain adequate strength and oxygen barrier properties.

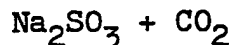
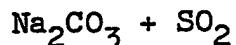
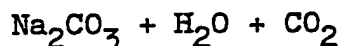
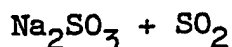
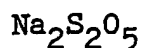
The blowing agent used in this series of experiments
25 was a mixture of sodium bicarbonate and sodium metabisulphite, the composition of the feedstock being:

30	Ethylene/Vinyl acetate copolymer	96%
	Sodium bicarbonate	1%
	Sodium metabisulphite	2%
	Pigment	1%

The sodium bicarbonate and the sodium metabisulphite decompose at the temperature to which the feedstock is heated prior to injection into the mould, to produce carbon dioxide, water vapour and sulphur dioxide and some
35 of the sulphur dioxide reacts with the sodium carbonate formed by decomposition of the sodium bicarbonate to liberate more carbon dioxide:-



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The sodium metabisulphite being present in stoichiometric
 5 excess, the blowing gas contains sulphur dioxide, carbon
 dioxide and water vapour which expand to cause foaming of
 the mixture as the feedstock enters the mould, the effect
 of the cool mould walls being to restrict the formation of
 cells at or near the surface of the moulded stopper, so
 10 that it has a closed-cell foamed core within a smooth
 liquid-impervious skin. The sulphur dioxide, carbon
 dioxide and water produced in the blowing process are
 retained in the cells.

There would be a tendency for the sulphur dioxide to
 15 diffuse slowly out of the cells if the stoppers were
 stored in air. They are therefore preferably stored in a
 sealed container in an atmosphere of sulphur dioxide until
 they are required for use.

Stoppers made as described above were coated with a
 20 polymethyl siloxane lubricant and inserted into the necks
 (of 19 mm internal diameter) of wine bottles using
 conventional cork-inserting machinery, in which the
 stoppers are compressed to a diameter of 15 mm before
 being inserted into the necks. The compressibility,
 25 resilience, creep resistance and frictional characteristics
 of the stoppers proved to be well suited to the machinery
 so as to enable the stoppers to be readily inserted and to
 cause them to grip the necks tightly and form effective
 and lasting seals with no tendency for the stoppers to
 30 slip out.

Measurements were made of the rate of oxygen
 diffusion through the stoppers described above, under
 normal atmospheric pressure conditions. Stoppers made
 with the 12½% and 15% VA copolymers showed figures of
 35 approximately 3 ml per annum in the first year. Stoppers
 of the 18% VA copolymer gave an average figure of 3.35 ml

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in the first year with a maximum of 3.5 ml in that year. After the first year, there was a drop to a rate of 2.5 ml per annum. These figures are well below the figure of 6.5 ml of oxygen which can be dealt with by the normal content of 50 p.p.m. free SO_2 in a mass-produced light table wine, indicating that a good shelf life could be expected. It will be understood that most other wines and wine-based products have a better resistance to oxidation so that even better shelf lives could be expected for such other products from use of stoppers in accordance with the invention.

By contrast, stoppers made in the same manner from various samples of ethylene/vinyl acetate copolymer having a vinyl acetate content of 28% were found to show oxygen diffusion rates of 6.6 ml per annum and higher and thus to have an unacceptably low oxygen barrier.

While the blowing agent described above is designed to produce sulphur dioxide and water in the cells to act as an oxygen scavenger and thus improve the oxygen barrier, it would naturally be possible to use other conventional blowing agents such as nitrogen, pentane, low boiling compounds such as methylene chloride or fluorinated hydrocarbons. Alternatively, sulphur dioxide and water can be produced in the cells by other blowing agents apart from the sodium metabisulphite and sodium bicarbonate mentioned above. For example, metabisulphites and bicarbonates of other metals, particularly other alkali metals such as potassium, may be used. The water vapour or part thereof may be provided by incorporation of hydrated sodium citrate in the blowing agent.

The stoppers may be moulded with a small chamfer at each end. Alternatively, they may be provided with a flanged end or head, e.g. of spherical or part-spherical shape, which may be moulded of the same EVA copolymer or of a different polymer.



CLAIMS

1. A closure for a container for a wine or wine-based product, at least the part of said closure which is intended to be exposed to the product being in the form of a moulded stopper of a thermoplastic material having a closed-cell foamed core within a liquid-impervious skin, characterised in that the thermoplastic material is an ethylene/vinyl acetate copolymer with a vinyl acetate content of from 10% to 25% and the degree of foaming of the moulded stopper, measured in terms of the reduction of density as compared with the unfoamed material, is from 45% to 70%.
2. A closure according to Claim 1, characterised in that the ethylene/vinyl acetate copolymer has a vinyl acetate content of from 10% to 20%.
3. A closure according to Claim 1 or 2, characterised in that the moulded stopper has a length of between 30 and 50 mm and an uncompressed diameter of substantially 22 mm and provides an oxygen barrier sufficient to restrict passage of oxygen into a container in which the closure is fitted to less than 4 ml per annum.
4. A closure according to any one of the preceding claims, characterised in that the cells of the foamed core contain sulphur dioxide and water enabling the sulphur dioxide to act as an oxygen scavenger.
5. A closure according to any one of the preceding claims, characterised in that the moulded stopper is coated with a silicone lubricant.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 80/00014

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. ³ B 65 D 39/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System ¹	Classification Symbols	
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹³
A	FR, A, 2349508, published November 25, 1977 see entire document, Metal Box Lim. --	1,4
A	FR, A, 2284534, published April 9, 1976 see page 1, lines 1-4, 17-26; page 2, lines 16-28, Le Bouchage Mecanique --	1
	DE, A, 2700259, published July 13, 1978 see claim 1, Müller -----	5
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IV. CERTIFICATION		
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9th April 1980	18th April 1980	
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